# XI. *On the Structure of Metals, its Origin and Changes.*

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[PLATES 9, 10.]

IT has been shown by HERBERT TOMLINSON that the atomic volume of metals is intimately connected with their thermal capacity* and with YOUNG'S modulus.† He considers in view of the work of WERTHEIM,‡ of MAXWELL,§ and of HEEN,‖ and as the result of his own experiments, that the value of the product of the elasticity E, when multiplied by a fractional power of the atomic volume, A/D, is a constant for all metals. $E\,(A/D)^{7/3} = 181 \times 10^4$. The divergencies shown by several metals from this mean value arise from the fact that the presence of small amounts of impurity makes a great difference in their elasticity.

SUTHERLAND¶ finds a close relation between the atomic volume and the rigidity of metals, and considers that this rigidity is "in its essence a kinetic phenomenon almost as simple in character as the elasticity of perfect gases."

Professor FESSENDEN,** moreover, has urged that the cohesion of metals is proportional to some power of the atomic volume, and he considers that the rigidity varies as the fifth power of the distance of the centre of the atoms, or as (atomic volume)$^{5/3}$. These facts are given merely to show that the atomic volume of the added element is very important.

Some years ago, one of us purified gold with great care and alloyed seventeen separate portions of it with foreign elements, in quantities which were in all cases close to 0·2 per cent., and from each sample of this alloyed gold, bars were cast 88 millims. long by 7·5 millims. wide by 5·2 millims. thick. The metal was in each case poured into a closed iron mould heated to about 500°; the cooling was therefore not very rapidly effected. The tensile strength, elongation, and reduction of sectional

* 'Roy. Soc. Proc.,' vol. 38 (1884–85), p. 488.
† 'Roy. Soc. Phil. Trans.,' 1883, p. 32.
‡ 'Ann. de Chim. et de Phys.,' vol. 12, 1844.
§ 'Roy. Soc., Phil. Trans.,' vol. 126, 1866.
‖ 'Bull. de l'Acad. Royale de Belgique,' vol. 4 (1882).
¶ 'Phil. Mag.,' vol. 32, 1891, p. 41.
** 'Chem. News,' vol. 66, 1892, p. 206.

area (striction) were determined, and the results given in the following table were published* in the Philosophical Transactions in 1888.

| Name of added element. | Tensile strength. | Elongation, per cent. (on 3 inches. | Impurity, per cent. | Atomic volume of impurity. | Reduction of area at fracture, per cent. |
|---|---|---|---|---|---|
| | Tons per sq. in. | | | | |
| Potassium . . | Less than 0·5 | Not perceptible | Less than 0·2 | 45·1 | Nil. |
| Bismuth . . . | 0·5 (about) | ,, | 0·210 | 20·9 | ,, |
| Tellurium. . . | 3·88 | ,, | 0·186 | 20·5 | ,, |
| Lead . . . . | 4·17 | 4·9 | 0·240 | 18·0 | Very slight. |
| Thallium . . . | 6·21 | 8·6 | 0·193 | 17·2 | 15 |
| Tin . . . . . | 6·21 | 12·3 | 0·196 | 16·2 | Not measured. |
| Antimony . . | 6·0 (about) | qy. | 0·203 | 17·9 | 54 |
| Cadmium. . . | 6·88 | 44·0 | 0·202 | 12·9 | See note † |
| *None.* Pure gold | 7·00 | 30·8 | *none* | — | ,, |
| Silver . . . . | 7·10 | 33·3 | 0·200 | 10·1 | ,, |
| Palladium . . | 7·10 | 32·6 | 0·205 | 9·4 | 75 |
| Zinc . . . . | 7·54 | 28·4 | 0·205 | 9·1 | 74 |
| Rhodium . . . | 7·76 | 25·0 | 0·21 (about) | 8·4 | See note † |
| Manganese . . | 7·99 | 29·7 | 0·207 | 6·8 | 60 |
| Indium . . . | 7·99 | 26·5 | 0·290 | 15·3 | 72 |
| Copper . . . | 8·22 | 43·5 | 0·193 | 7·0 | See note † |
| Lithium . . . | 8·87 | 21·0 | 0·201 | 11·8 | 60 |
| Aluminium . . | 8·87 | 25·5 | 0·186 | 10·45 | 46 |

These results indicated, in a general way, that the tenacity and ductility of gold is increased by the presence of 0·2 per cent. of an added element of smaller atomic volume than that of gold itself, while on the other hand, these properties are diminished when the atomic volume of the added element is greater than that of gold. There are, as might be expected, exceptions and irregularities, but it is strange that they are not more numerous and more marked. The weight of the added element is in all cases close to 0·2 per cent., but the atomic percentage differs widely. It will be interesting to ascertain in a future research, what is the effect of adding to gold equal numbers of atoms of foreign elements.

The investigations which have been conducted in later years have revealed the complexities of the question. Even the purest metals are not, from a mechanical point of view, homogeneous. Under the influence of internal forces which tend to make them crystalline, and of external stresses which are set up by contraction during cooling, the invisible molecules become arranged in visible and more or less highly organised groups. These groups are separated from each other either by planes of cleavage or by joints which are often surfaces of least cohesion, and therefore of weakness. This is especially the case when these joints have been accentuated by the evolution of dissolved gas at the moment of the solidification of the metal.

In alloys, chemical homogeneity may, in turn, disappear, and free metals, chemical compounds, or various alloys, may fall out of solution from the liquid mass and finally

* 'Roy. Soc. Phil. Trans.,' vol. 179, 1888, A, p. 339.

† These test-pieces drew out after the manner of pitch, that is, as a viscous solid.

the *eutectic* alloy solidifies, but the presence of a residual fluid facilitates the arrangement of the parts which have previously solidified.

One of us, in collaboration with M. WERTH,* was probably the first to direct attention to the influence which these fusible residues, to which the name of "cements" was given, could exert on the working of steel and on the mechanical properties of the finished products. Since then, M. ANDRÉ LE CHATELIER† has repeatedly insisted on this point, correctly enough as a principle, though perhaps with a tendency to generalise too much from ideas which are in themselves accurate. The Reports of the Alloys Research Committee, organised by the Institution of Mechanical Engineers,‡ have, by the aid of autographic curves of the cooling of alloys, brought into prominence a certain number of instances of liquation in the cases of copper and silver, copper and bismuth, gold and aluminium, copper and tin.

Micrographs also reveal the existence of numerous constituents in a great number of alloys; in an alloy of 78 per cent. of gold with 22 of aluminium for instance, grains of a definite compound $Au\,Al_2$, of a brilliant purple colour, are separated by a fine network of a white alloy of very different composition,§ and numerous other analogous examples are to be found in the work of BEHRENS,‖ of GUILLEMIN,¶ of CHARPY,** and others.

In short, we are led to distinguish in metals and alloys both the *visible* structure and the *molecular* structure, and, between these, such methods of investigation as are possible, enable a well-defined line of demarcation to be traced. Attention must therefore be directed to ascertaining to what extent the mechanical properties of a given sample of metal are due to each of these kinds of structure, and how far to such relations as are possible between them. This being the case, we considered that it would be interesting to submit the gold, containing 0·2 per cent. of various elements, to micrographical examination, and, fortunately, the identical specimens, which were submitted by one of us to the Royal Society eight years ago, had been preserved intact, and were available for examination.

Gold is a metal which may readily be purified to a high degree. It does not oxidize in air at any temperature. The influence of occluded gases appears to be small; and the quantity of the added element is in each case so small as to favour the view that, at least, most of the impurity remains dissolved throughout the mass without there being liquation either of definite or indefinite compounds. We have, in fact,

* OSMOND and WERTH, "Ann. des Mines," vol. 8, 1885, p. 5.

† "Proc. Inst. Mech. Engineers," April, 1893, p. 191.

‡ *Ibid.*, October, 1891, p. 543; April, 1893, p. 102; April, 1895, p. 238.

§ This observation was not printed, but a diagram of the section was shown at a lecture delivered at the Royal Institution, 1891, and has been continuously used since by one of us in class teaching.

‖ "Das Mikroskopische Gefüge der Metalle und Legierungen," Leipzig, Voss, 1894.

¶ "Commission des méthodes d'essai des matériaux de construction," T. II., p. 19.

** "Bull. de la Soc. d'Encouragement," February, 1896.

reason to think that many disturbing causes are, if not eliminated, at least reduced to a minimum in this series of alloys. It will be possible up to a certain point to apportion the effect of these disturbing causes, and eventually to set aside such complications as tend to conceal the effect of atomic volume in the researches to which reference has been made.

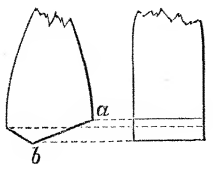
With the exception of some facts stated by BEHRENS, and of some early experiments of our own, on the alloys of gold and aluminium, to which we have just referred, Professor ARNOLD was the first to examine the alloys of gold. He took the experiments of one of us on the influence of impurities on the mechanical properties of gold as the basis of his work,* and made some careful drawings of etched sections of pure gold alloyed with about 0·2 per cent. of various impurities. We consider, however, that photographs of micro-sections are far preferable to drawings, and we agree with M. CHARPY,† in thinking that drawings, however careful, give a very incomplete idea of the appearance of etched metallic surfaces. We have therefore great pleasure in submitting to the Society micro-photographs from the identical specimens of gold described by one of us in 1888, which formed the starting point for the later investigations. The results of the micrographic examination of these specimens of gold forms the first part of the present paper.

## PART I.

The alloys examined may be conveniently represented by the chemical symbol of the metal added to the gold, which was in each case in the proportion of 0·2 per cent. They are the twelve following: K, Bi, Zr, Rh, In, Li, Se, Zn, Pd, Te, Sb, Al. Thus "K" would signify gold containing 0·2 per cent. of potassium and so on. It will also be convenient to supplement this series by a sample of pure gold which was cooled under precisely the same conditions as the "test pieces" into which the alloys submitted to mechanical tests were cast.

These test pieces had been divided by two chisel cuts close to the part which had been restricted by traction, so that the portions which were preserved resembled the form shown in fig. 1. The structure would have been examined on a section at right angles to the axis of the bar, but this method of procedure proved to be inconvenient, as it did not make the most of the precious metal, and it would have notably diminished the dimensions of the fragments, which were already too small to be conveniently handled. It was necessary, therefore, to be content with rubbing the face $a$ $b$ on emery paper until it became flat, hence the sections are oblique in relation to the axis of the bar. We should have preferred to examine bars which had not been distorted by traction, but it was important to use the old specimens which were available.

Fig. 1.




* 'Engineering,' vol. 61, 1896, p. 176.

† 'Bull. Soc. d'Encourage,' vol. 1, 1896, p. 200.

*Polishing.*—Even the finest emery paper tears the metal and produces relatively deep scratches. These are effaced by the use of *Brillant Belge*, a commercial product of which the exact composition is unknown, though it is widely used by jewellers, as well as for domestic use in cleaning copper. This *Brillant Belge* is spread on a sheepskin covering a revolving plate; it, however, leaves scratches. The polishing is continued with English rouge of the best quality, prepared by the calcination of pure oxalate of iron, as prescribed by M. HENRIVAUX. This rouge is spread dry in small quantities on chamois leather covering, as in the case of the *Brillant Belge*, the surface of a revolving disc. In order to polish successfully, a certain lightness of hand is necessary, otherwise the rouge scratches and soils the surface of the gold; with a little practice, however, a polish which appears very beautiful to the naked eye may be obtained, but it is nevertheless imperfect. This may be seen from photographs 15 and 16, where the principal mass of the metal is not etched or hardly so. There are a few large, purely accidental scratches which give no trouble, while the surface remains finely striated. We have not succeeded in doing better by this treatment; gold is very soft and it spreads without receiving a polish when such powders are employed as do not actually scratch it. It is, moreover, very difficult to prepare powders in a sufficiently pure state to exclude all traces of gritty constituents, but this relative imperfection of the polishing is in some respects advantageous and affords a method of investigation which has been successfully employed in other circumstances. If the impurities in the little section under examination have become concentrated in compounds which have liquated from the mass, these are generally harder than the pure gold, and their presence will probably be revealed by a more mirror-like polish. Further, polishing on a soft substance like chamois leather, will cause these liquated portions to appear in relief. Finally their colour in certain cases differs more or less from that of gold, and enables them to be distinguished from the mass.

We have insisted upon the indications furnished by polishing, as they are often very useful in metallography, by enabling a constituent to be defined. The sunk lines, which may be the result of a general attack by etching (or attacking the section with a reagent) are in themselves by no means characteristic of the presence of a free constituent in the mass. In default of the additional evidence afforded by polishing, they probably represent lines of minimum compactness, along which the etching is deeper, or even, according to Commander HARTMANN, lines of tension.*

In fact, polishing revealed some cavities which were relatively important in gold alloyed with bismuth, thallium, or potassium. In this last case, and especially in the alloy with indium, we observed grey filaments, which were possibly due to the incorporation of traces of rouge in a network of fissures, although they might also be attributed to the presence of a cement, and in all cases they deserved attention.

*Partial Attack.*—It is known that certain alloys of gold, especially those with iron,

* 'Distribution des déformations dans les métaux soumis à des efforts;' Paris, BERGER-LEVRAULT, 1896.

zinc, copper, lead, silver, &c., are attacked by certain acids which do not attack the gold itself.* This fact led us to hope that the use of suitable reagents would afford useful data. Pure nitric acid (spec. grav. 1·33) was without action in the case of twelve of the specimens which were subjected to its action for five minutes at a temperature close to its boiling point, but it developed, on the section of the alloy with indium, a network of either dotted or continuous lines, to which we shall again refer after we have described the results of a general attack by *aqua regia*. This observation confirms the indications afforded by polishing, and puts beyond question the existence of a cement in the alloy of gold with indium, and this alloy has not been submitted to the action of other reagents which attack it partially (see photo. 18).

If the alloys were kept boiling in pure hydrochloric acid for five minutes, no result was produced. In a preliminary trial, where the specimens had not been previously perfectly cleaned, the rouge adhering to their surfaces was converted into ferric chloride, and all the sections were slightly tarnished. When these conditions prevailed only the alloy of potassium showed a black polygonal network *in intaglio*.

Sulphuric acid (spec. grav. 1·84) is supposed to be without action upon gold. On heating our alloys, however, for five minutes, followed by a treatment for ten minutes, at a temperature at which white fumes were evolved (200–250°), the acid became tinted and the specimens were slightly attacked.† Their polish was, nevertheless not materially diminished, but the greater part of them showed a network of fine lines of nearly uniform width, and without special coloration (see Plate 10, photo. 16).

As these lines presented exactly the same characters in pure gold and in the alloys, it is evident that they do not afford an indication of the presence of a cement. They are joints of contiguous grains. But we will examine this question of joints later in detail. For the moment we would only note the following exception. In the case of the alloy with potassium, instead of a network of sunk joints, the network seemed to be in slight relief corresponding to that which had already been revealed by the action of impure hydrochloric acid. We have, therefore, three indications which taken separately are slender; but they are concordant, and point to the probability of the existence of a cement in the alloy in question.

*General Attack by Reagents.*—The polished surfaces were immersed three times in *aqua regia* (half hydrochloric, half nitric acid), the temperature being a little below boiling point, until effervescence began, that is to say, after about seven seconds each time.‡ Micrographic examination afforded the following results :—

* 'L'or,' par Cumenge et Fuchs; Paris, Dunod, pp. 96–102; 'Encyclopédie chimique de Frémy.' H. Louis, 'Trans. of the Amer. Inst. of Min. Engineers,' vol. 24, p. 705 (1894).

† The absence of nitrous derivatives was verified by testing by ferrous sulphate.

‡ Other attempts have been made to attack the alloys attached to the positive pole of a weak battery, by a dilute solution of cyanide of potassium (3·5 of the solid salt in 100 of water), but this reagent taught nothing more than *aqua regia* and was abandoned.

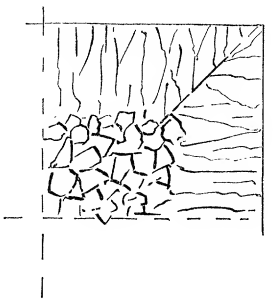
1. First a general structure, visible under small magnification (twenty diameters for instance), and sometimes even to the naked eye. This structure is that of ingots of steel, and, probably, also of most metals which have been poured in ingot moulds.

The mass subdivides itself into jointed groups, the intimate nature of which we will consider later, but the groups may be distinguished from each other either by a different general orientation of elementary crystallization, or by being more or less energetically attacked (see Plate 9, photos. 1, 2, 3, 4, 5, 6). It follows from this that the same group may appear either brilliant or dark, golden, brick-red, or deep purple, according to whether it reflects more or less light into the objective under a definite mode of illumination. The photographs 1 and 6, for instance, represent the same micro-section lighted obliquely, but from opposite directions. The general orientation is, however, subject in a given group to local changes (photo. 12), but the limits of the subdivisions are then ill defined.

If we eliminate the complications introduced into our observations by the obliquity of the sections, and by the deformation of the test pieces caused by traction, it will be seen (photos. 1, 2, 3, 4, 5) that the groups are of two kinds, and resemble those which CHERNOFF found in ingots of steel.

Those at the periphery are prismatic and at right angles to the surface of cooling; while those in the interior are, roughly speaking, equi-axial, so that a transverse section of a quarter of an ingot may be diagrammatically represented by fig. 2. The genesis of this double structure has already been explained by one of us in a paper on the "Cellular Theory as applied to Metals."*

Fig. 2.



The absolute dimensions of the groups, and the relative importance of prisms and equi-axial polyhedra, vary in ingots of steel with the rapidity of cooling, with the temperature of the metal at the moment of pouring, with the amount of occluded gas and with chemical composition. We have detected in our alloys of gold analogous variations. From this point of view, the thirteen specimens may be divided into five classes, of which each is represented by a photograph in which the micro-section is enlarged to seventeen diameters and illuminated obliquely by SORBY'S parabolic mirror.

First, the prisms are of considerable size and occupy the whole section, even to the centre (Au, Bi, Zr, Rh, Zn, Pd, Tl; see photos. 1 and 6).

Second, the prisms do not occupy all the mass, their mean size is smaller than that of the metals in the first category, and a central core is occupied by polyhedra, which are roughly equi-axial (Li, Se; see photo. 2 of the alloy with lithium).

Third, the prisms stop about midway between the periphery and the longitudinal axis of the section, while the central core becomes of considerable importance (In, Sb, see photo. 3 of alloy with indium).

* 'Ann. des Mines,' 8th Series, vol. 8, pp. 5–84.

Fourth, the border of prisms become restricted and the polyhedra dominant; both prisms and polyhedra being of small size (K; see photo. 5).

Fifth, the distinction between the groups is very slight (A1; see photo. 4). This is only true for rather more than half of the section, the rest of it would be more fittingly placed in the second category.

The question arises—are the differences which we have signalised caused solely by the difference in the composition of the alloys, or can they to some extent be attributed to variations in the experimental conditions under which the bars were prepared, such variations, for instance, as those which occurred in the temperature of the metal at the moment of pouring? We cannot as yet tell. It is, however, certain that there is no relation between either the structure of the mass, the appearance of the fractures, the melting point of the alloyed elements, and the mechanical properties given in the table on page 418.

Every iron metallurgist who sees our photographs will probably think, at first sight, that the alloy with potassium (photo. 5) will possess the best mechanical properties and that the structure indicated by photograph 1 is deplorable.

The fact is that from a mechanical point of view the alloy of gold with potassium is the worst of all the series, and photograph 1 might equally well represent alloys which vary in tenacity from less than half a ton per square inch to 7·75 tons per square inch, and either are incapable of being stretched or may be elongated 32·6 per cent.

There remains to be considered the groupings (polyhedral or prismatic), from the triple point of view of their external form, their internal structure, and their mutual relations in the neighbourhood of each other.

II. Hitherto we have advisedly employed the vague term "groups" to designate the patches which are differentiated on the etched section by variations of colour and lustre.

This is because we are uncertain as to the true nature of these groups, and it appeared useful to preserve a distinction which is ordinarily ignored between crystals which are defined by natural characteristic inclinations, and the *pseudo* crystals which have been arrested in a more or less haphazard way in consequence of the independent growth of neighbouring groups.* The latter groups have already been called "cells" or "grains," but the word grains appears in this case to be more suitable, in view of the fact that interposed foreign matter is usually absent.

Microscopical examination, with a moderate enlargement of 100 to 300 diameters, enabled us to see the parts respectively played in our alloys by crystals and by grains. Pure gold when alloyed with 0·2 per cent. of bismuth, zirconium, rhodium, zinc, palladium or thallium, is entirely formed of grains. The gold alloyed with lithium or selenium only contains grains in the prismatic envelope, while in the interior the grains have a tendency to pass to crystallites, and the result is mixed jointing, with

* The substance of the mass may, however, be crystalline.

complicated sutures analogous to those in cranial bones. This tendency is still more marked in the alloys with indium and antimony, especially in the interior, but it is visible in the prisms at the periphery (photo. 14). The alloy with potassium is a curious mixture of little grains, of perfectly defined crystallites, and of mixed forms (photo. 11). The appearance of certain portions of the alloy with aluminium approaches that of the alloys with lithium and selenium, but the bulk is rather crystalline.

III. The interior paste, whether it be in grains or crystallites, is certainly crystalline, as might have been anticipated from the fact that the colour of the grains varies with the incidence of the light. When examined, after etching, under an enlargement of 1000 diameters, this paste presents three aspects :—

(*a*) Clear vermicular structures on a dark ground.
(*b*) Parallel grooves.
(*c*) Pointed crystals of the same orientation, in lines nearly parallel.

The photographs 21, 9, and 10 show these different aspects, which, it must be remembered, do not correspond with true differences of structure, but with different sections of a single structure. As far as it is possible to judge, it is a question of files of little crystals penetrating each other, the general orientation of which remains constant in the area of each grain.

In this paste, resulting from primary and rapid crystallization, which constitutes the principal mass of the greater part of our alloys, some small secondary crystals separate themselves with relative distinctness. These are probably small cubes, the diameter of which is about 2·5 $\mu$ ; they have a tendency to range themselves in groups and pass progressively into crystallites by a series of intermediate stages, which it is easy to follow through the whole series of the specimens, and thus to connect one with another.

During the course of this secondary crystallization five stages or classes can be distinguished, and each can be designated by a number :

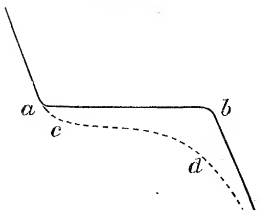
0. Absence of little crystals (photo. 10, pure gold ; 1000 diameters).
1. Small detached crystals isolated indiscriminately.
2. Small crystals in rows at regular intervals (photo. 14, in which the magnification is 150 diameters, and 17, 500 diameters).
3. Small connected crystals, often joined in parallel lines, in which they may lose their individuality, and are illustrated by the same photos. as in Class 2.
4. The parallel lines thus formed become aggregated crystallites (photo. 13, Al, 150 diameters).

None of the specimens belong exclusively to a single class, as one part of a section represents a certain class and the rest of it another, but in a given section the secondary crystallization attains certain limits which it does not exceed, and among these five classes our thirteen specimens are distributed as follows :—

Between Classes 0 and 1 : pure gold, alloyed with Bi, Zr, Rh, Pd, Zn.
„ „ 0 „ 2 : alloys with Tl, Sb, Se.
„ „ 0 „ 3 : „ „ K, In.
„ „ 1 „ 4 : „ „ Li, Al. A large portion of the alloy with aluminium belongs entirely to type 4.

This more or less accentuated development of a secondary crystallization is, in itself, interesting in connection with the phenomena observed by one of us* in the curves which represent the solidification of gold (fig. 3). In the presence of small quantities of lead, or of certain other bodies, the horizontal portion of the curve, which represents the actual solidification of the metal, is not sharp at its angles as shown in the line $a$, $b$, but is rounded as at $c$, $d$, and is often inclined at an angle to the datum line. This points to the existence of a transitory pasty state which may facilitate the secondary crystallization.†

Fig. 3.




It may be asked whether the small crystals above-mentioned, and their aggregates do not represent an allotropic form of gold.‡ Some explanation may thus be afforded of the mechanical properties of the alloys of gold with 0·2 per cent. of aluminium, and of gold with 0·2 per cent. of lithium, which are, at the same time, the most tenacious and the most perfectly-crystallized of the entire series. But, on the other hand, this same kind of crystallization connects the alloy of gold and bismuth, for instance, with the alloy of gold and rhodium, these being the members of our series which are very wide apart from the point of view of tenacity and extensibility.

It must be admitted, moreover, that the influence of the secondary crystallization on the mechanical properties of the alloys, supposing it exists, is at least greatly complicated by some other more powerful influence.

IV. It only remains for us to consider the relations which result from the association of contiguous grains or crystallites, that is to say, from their surfaces in contact, or joints. The general crystalline orientation of the paste on both borders of the joint is not the same, and the elementary crystals belonging to two different groups may not be as firmly united as they would be in the interior of a homogeneous group ; a joint, therefore, becomes a surface of weakness (sometimes passing progressively into a fissure), which etching by a reagent enlarges and renders visible. In fact, all our etched surfaces are divided by a network of joints, which correspond with the outlines of the grains and crystallites.

The joints revealed by the action of sulphuric acid are simple furrows, which occur

* 'Proc. Inst. Mech. Engineers,' Oct. 1891, p. 558–564.

† Secondary crystallization is at a minimum in the case of pure gold.

‡ Compare the notes of H. Louis on "The Allotropism of Gold," and "Further Experiments on Amorphous Gold," 'Trans. Amer. Inst. of Mining Engineers,' vol. 24, pp. 182 and 705, 1894.

in all our specimens, except in the alloy with potassium.* When revealed by the action of *aqua regia*, these joints usually appear under the microscope as being of a brick-red or deep purple colour, and are of variable thickness. In certain cases they are only mathematical lines, that is to say, without thickness, and their existence is only revealed by the different coloration of the grains of which they form the limit (see photos. 12, Rh, 150 diameters; and 9, Rh, 1000 diameters). In other cases, the joints revealed by etching have a definite thickness (see photos. 15, Tl; 14, In; 11, K; 150 diameters). These joints, which are more or less thick, when carefully examined under high magnification, may be represented by two types. One of these is formed of a sunk line, generally very fine, on the edges of which crystals, apparently little cubes, are ranged, which are secondary crystallizations. These are sometimes isolated, but more usually run together, and are joined in continuous files (see photo. 17, In, 500 diameters). Other joints are simply constituted by the separation for a short distance of primary crystals, between which the acid can penetrate more easily and etch away a deeper channel. We will call the latter, as distinguished from the former, *non-crystalline*.†

Considered from the point of view of the nature and the thickness of their joints,‡ our thirteen specimens may be divided into five groups.

1st. Pure gold; alloys with Zr, Al, Rh, Pd, Zn; joints which are usually non-crystalline, of a thickness which equals 0 to 2 $\mu$ ($\mu = 0{\cdot}001$ mm.), the mathematical joints or very fine ones are dominant.

2nd. Alloy with lithium; the thickness of the joints equals 0 to 3·5 $\mu$; the thick joints are crystalline but are rare and disconnected, the mathematical joints, or very fine joints are dominant.

3rd. Alloys with Sb, Se; crystalline joints which are often broken; the thickness of these equals 1 $\mu$ to 3·5 $\mu$, or a mean thickness of 2 $\mu$.

4th. The alloys with In, K; crystalline continuous joints, with a thickness of 1 to 4 $\mu$, or a mean thickness of 2 to 2·5 $\mu$.

5th. Alloys with Tl, Bi; crystalline joints, which are continuous, often passing into

* The alloy of gold and indium has not been etched by sulphuric acid.

† It may be well to record an appearance which is sometimes met with, and may lead to error. Certain thick non-crystalline joints simulate the presence of an interposed cement, for, on account of the difference of level between the depth of the joint and the surface, shadows are cast. This is most clearly shown by the photograph 10 (1000 diameters). The plane etched by *aqua regia* had not been repolished after the previous etching by sulphuric acid. It looks as if a film of foreign substance was interposed between two neighbouring grains, but, on looking at it closer, it is evident that the traces of this film join those of one of the grains, and it is not possible to admit a doubt that we have merely to deal with the structure of pure gold.

‡ By the expression "thickness of a joint," we understand, in the case of the crystalline joints, the sum of the joint properly so-called, and of the crystalline border, which it is usually impossible to separate from it. We have, in fact, measured in all cases the thickness of the dark line. It must not be forgotten that it is a question of the apparent dimensions, which are much exaggerated by the etching.

fissures, the thickness equals 1 $\mu$ to 5 $\mu$, or a mean thickness of 2·5 $\mu$. Generally speaking the condition of these joints appears to be closely related to the mechanical properties of the alloy (table, p. 418.).

*Conclusions.*—We do not contest in any way, as our previous publications abundantly prove, the importance of the part which may be played in the mechanical properties of the alloys by the residues which remain liquid after the main mass of the alloy has solidified, the alloys being tested either at the ordinary temperature or when heated. But, in order that it may be possible for such cements to intervene and affect the mechanical properties of alloys, the cements must at least have a real existence. Nothing indicates that they do exist in ten out of twelve of our alloys, but we would not even express ourselves too positively on this point, for some new method of etching may reveal new facts. The impurities which are sought for may happen to concentrate themselves beyond the particular region which has been sectioned. These are, however, for the present gratuitous suppositions. Polishing only indicates the presence of cement in two cases. The little secondary crystals which we have already described might readily be mistaken for cements of definite or indefinite composition if they were found only in certain specimens and then in such proportions as could be accepted. But we meet with them everywhere and in all cases their appearance is constant in forms and dimensions, and moreover we see them collect into crystallites which pervade the whole mass. These crystals are therefore usually and indubitably due to the crystallization of gold itself, although the alloying substances sometimes (indium and probably potassium) join up the crystals in question. For the same reason the dark lines of the joints, traced as furrows by the etching, are very rarely the empty tracks of cement which has been dissolved away by *aqua regia*; their formation, which it is easy to follow in all its phases, directly connects them with secondary crystallization. We are led to the belief that in the case of ten of our alloys of gold with about 0·2 per cent. of various impurities, solidification of the whole mass, although prolonged and less rapid than in the case of pure gold, has been directly accomplished without interruption, and that the foreign bodies have remained partly or wholly as *solidified* solutions, the impurities being dissociated into their atoms in both solid and liquid. We can at least say, without going beyond the actual evidence before us, that the dissemination of the foreign bodies eludes the power of the methods of investigation which we have employed. Under these conditions it is difficult to invoke, as explaining the mechanical properties of the alloy, the intervention of hypothetical cements with relatively low fusing points.

The absolute dimensions of the grains or crystallites cannot, as we have already seen, account for the mechanical properties. The micrographic examination of the copper-zinc alloys (brasses) has recently led M. CHARPY* to a similar conclusion, and it is now certain that the large size of the grains does not, in itself, constitute a

* *Loc. cit.* He also shows that ordinary brasses may be effectively annealed at 500°.

defective or an undesirable form of structure. If the metallurgy of steel points to a different conclusion, it is probably owing to the presence of gases which are often abundant and are apt to accumulate between the grains; these gases are the less divided, and consequently are the more dangerous, when the grains are large and the total surface of the joints is small for a unit of volume. Our attention has been specially directed to this point of M. WERTH, who justly attaches great importance to the question of the presence of gas in steel.

The more or less advanced state of the crystallization compared with the results of the tests for tensile strength does not show any direct relation.

Finally, micrographical examination only leaves us the joints themselves to account for the observed mechanical properties. Here the concordance is fairly good.* Without wishing to attribute a degree of precision which does not belong to them to the dimensions of joints which have been widened by etching, and perhaps modified to some extent by the longitudinal stress to which the bars were subjected, we can readily see, in a general way, that the thick and crystalline joints correspond to the alloys of low tenacity, while the converse is also true. But if the mechanical properties are in direct relation to the thickness of the joints and to the atomic volume of the alloyed elements, we may fairly conclude that a relation of cause to effect should exist between these two last variables.

This conclusion appears rather unforeseen. If we seek its interpretation, we are face to face with a very important but very complex question, that of the genesis of the joints in the metal.

A joint is often a surface of weakness, as we have already stated, in that it alone marks a sharp change of organization and constitutes the artificial border of two natural groups. The more it diverges from a mathematical surface and acquires sensible thickness the weaker it becomes. How, then, is a joint formed? Evidently by an internal stress, if occluded gas, which appears negligible in the case of gold, be left out of the question. Such tractional stress is produced during solidification, cooling and consequent shrinkage (and sometimes experimental proof of it is found in the presence of scraps of metal attached to the edges of a fissure). In order that a joint may be opened it is necessary (and it is enough) that the joint should be subjected, at a given moment, to a greater weight than its breaking strain, and that this breaking strain is less than the elastic limit of the metal in the interior of the grains.

We have then four factors at work:

1. The stresses established by the change of volume of the metal when it solidifies.

2. The stresses established by shrinkage, which themselves depend (the conditions of cooling remaining constant) on the coefficient of expansion of the metal.

3. The elastic limit and the "*deformability*" of the metal which forms the body of the grains.

* The alloy with indium is an exception, but we have verified the presence of cement which has had, in this case, a favourable influence on the mechanical qualities.

4. The strength of the joint, which is *nil* towards the end of the solidification, and remains insignificant for a longer time if the solidification is prolonged by the presence of impurity in the way indicated in fig. 3. The presence of a crystalline envelop covering the joints, which appears to be an unfavourable condition, as it is specially marked in the alloys of low tenacity, is probably also connected with the prolongation or want of sharpness in solidification occasioned by the presence of certain foreign bodies. These envelopes without doubt represent the parts which have solidified last.

But all the factors we have just reviewed co-operate directly in determining the condition of the joints, and indirectly the mechanical properties of the cooled metal. The co-efficient of expansion, the elastic limit and plasticity of the bodies of the grains and the delayed solidification) are directly dependent on the molecules and atoms. It is therefore not surprising that in a case which is relatively so simple as that of gold the influence of the atomic volume of the added elements can be directly observed. Furthermore, the relation between the mechanical properties of the metals and the atomic volume of the dissolved impurities is an experimental fact. We can now explain the greater part of the apparent exceptions. The exceptional behaviour of indium is explained by the presence of a cement, and that of lithium and of aluminium by the development of secondary crystallization.* But as the conversion of heat into work is effected in the steam engine by a series of intermediate stages, so here also a more or less complex mechanism intervenes between the extreme terms which are in relation to each other. The foregoing research is a small contribution to the study of one of the elements of this mechanism.

## Part II.—On some Phenomena of Annealing.

Etching by sulphuric acid at a temperature of between 200° to 250° revealed a network of joints on the gold alloyed with bismuth and thallium, which the previous attack with *aqua regia* had not rendered apparent. All the specimens (except the alloy with indium which had not been subjected to the action of sulphuric acid) were then repolished and again etched with *aqua regia* under the same conditions as before.

The pure gold and the alloys with K, Pd, Zn, Rh, Li, Se, and Zr did not undergo any change, but the appearance of the four alloys with Bi, Tl, Sb, and Al were more or less altered by the treatment.

The bismuth alloy, which was initially adequately represented by the zirconium-gold, Photograph No. 6, for a magnification of 17 diameters, and by the thallium-gold, Photograph No. 15, which shows details (magnified 150 diameters), is now represented by Photographs No. 7 (17 diameters) and No. 20 (150 diameters). The large grains of the melted metal become sub-divided, after heating for five minutes to between 200° to 250°, into a number of small polyhedral grains. The effect is just

* Zinconium still presents a very striking exception.

the same as is caused by annealing steel castings at a temperature of about 800°. Nothing remains of the original structures. In the new grains the paste, the secondary crystallization, and the joints present the same characteristics as in the old grains.

The alloy with thallium undergoes a strictly analogous transformation, but the dominant lines of the initial structure have been preserved in several places, notwithstanding the internal rearrangement (photo. 19, 150 diameters). The alloy with antimony behaved in a very different fashion; this alloy, which was adequately represented before annealing at 200° by the gold-indium, photograph 3 (17 diameters) and by 14 for the details (150 diameters), is now represented by the photographs 8 (17 diameters) and 22 (150 diameters). The original structure has disappeared, but the new organization shows neither the polyhedral grains nor the continuous network of joints; the incipient grains, indicated by the crystalline orientations, have not clean faces, and the sulphuric acid only traces fragments of broken joints. This structure recalls that of hardened steel of medium hardness.

The alloy with aluminium undergoes the same transformation, but only locally and partially. Generally speaking, it seems that bismuth, thallium, antimony, and aluminium, when present in the proportion of about 0·2 per cent., behave in respect to gold in the same way as carbon does with regard to steel, but at a much lower temperature.

It also appears to be evident that the bodies in question must have been present in the solid metal in a state closely resembling the fluid. None of these bodies possess a very high melting point, and, as is natural, this circumstance favours the maintenance of fluid molecules at a low temperature. The temperature, however, of annealing remains much below that of melting aluminium or antimony, and even below the melting points of the *eutectic* alloy of aluminium and gold (about 600°) or of antimony and gold (440°), and it at most reaches that of the fusion of bismuth. On the other hand, lithium, with a point of fusion below that of bismuth, and zinc with a fusing point below that of antimony, have not exerted a similar effect in lowering the temperature of annealing.* The melting point of the impurities, although it is not without influence, is not the sole factor to be considered. It should be observed that lead, judging from what is known of its action on gold, probably behaves like bismuth and thallium. Amalgamation also appears to be a phenomenon of the same kind, possibly occurring, owing to the liquidity of mercury, at a still lower temperature. But gold, mercury, thallium, lead, and bismuth follow each other in the classification of elements based on increasing atomic weight, and are grouped on the same horizontal line of MENDELEEF'S table. This coincidence is curious. Whatever it may signify, this transformation of the structure of a metal, at a temperature so far below its melting point, in the presence of only two-tenths per cent. of a foreign body, is probably not an isolated fact, and appears to open a new field for research.

* We are not speaking of potassium, which appears to be concentrated in a cement.

## Description of Plates 9 and 10.

| Number of micro-section. | Description of specimen. | | Reagent by which the section was etched. | Method of illumination. | Enlargement, linear. |
|---|---|---|---|---|---|
| | Gold alloyed with 0·2 per cent. of | Treatment of the alloy. | | | |
| 1 | Zirconium | Poured in a mould | Aqua regia | Oblique | 17 |
| 2 | Lithium | ,, ,, | ,, ,, | ,, | 17 |
| 3 | Indium | ,, ,, | ,, ,, | ,, | 17 |
| 4 | Aluminium | ,, ,, | ,, ,, | ,, | 17 |
| 5 | Potassium | ,, ,, | ,, ,, | ,, | 17 |
| 6 | Zirconium | ,, ,, | ,, ,, | ,, | 17 |
| 7 | Bismuth | Annealed at about 200° to 250° | ,, ,, | ,, | 17 |
| 8 | Antimony | ,, ,, | ,, ,, | ,, | 17 |
| 9 | Rhodium | Poured in a mould | ,, ,, | Normal | 1000 |
| 10 | Nothing (pure gold) | ,, ,, | ,, ,, | ,, | 1000 |
| 11 | Potassium | ,, ,, | ,, ,, | ,, | 150 |
| 12 | Rhodium | ,, ,, | ,, ,, | ,, | 150 |
| 13 | Aluminium | ,, ,, | ,, ,, | ,, | 150 |
| 14 | Indium | ,, ,, | ,, ,, | ,, | 150 |
| 15 | Thallium | ,, ,, | ,, ,, | ,, | 150 |
| 16 | Nothing (pure gold) | ,, ,, | Sulphuric acid | ,, | 150 |
| 17 | Indium | ,, ,, | Aqua regia | ,, | 500 |
| 18 | Indium | ,, ,, | Nitric acid | ,, | 150 |
| 19 | Thallium | Annealed at about 200° to 250° | Aqua regia | ,, | 150 |
| 20 | Bismuth | ,, ,, | ,, ,, | ,, | 150 |
| 21 | Bismuth | ,, ,, | ,, ,, | ,, | 1000 |
| 22 | Antimony | ,, ,, | ,, ,, | ,, | 150 |

### Notes.

Photograph No. 1 would represent equally well either gold alloyed with Bi, Rh, Zn, Pd, Tl, or pure gold prepared under the same conditions.

Photograph No. 2 would also represent gold alloyed with Se, and poured in a mould; while No. 3 would represent gold alloyed with antimony.

Photograph No. 11 shows a mixture of grains and crystallites, a secondary crystallization belonging to classes 0 to 3 with thick crystalline joints.

Photograph No. 12 presents a characteristic case in which crystallites are absent; there is no secondary crystallization, and there are very fine non-crystalline joints.

Photograph No. 13 shows the complete development of secondary crystallization, with variable and disconnected joints.

Photographs Nos. 14 and 17 show the intermediate stages of secondary crystallization, the joints being thick and crystalline.

Photograph No. 15 shows a very thick joint crossing a paste of primary crystallization.

Photograph No. 16 shows the general aspect of joints, which would be traced by sulphuric acid on most of the specimens.

Neither these photographs (11 to 17) nor photographs 1 to 6, 9, 10, and 21 are characteristic only of the alloys from which they were taken; they have been chosen as typical illustrations of the organization of primary crystallization, of the variable development of joints, and, in fact, of the general phenomena which have been described in the text.

Photographs 7, 8, 19, 20, and 22 are of a more special nature; they show the effects of annealing at a given temperature on a given alloy.

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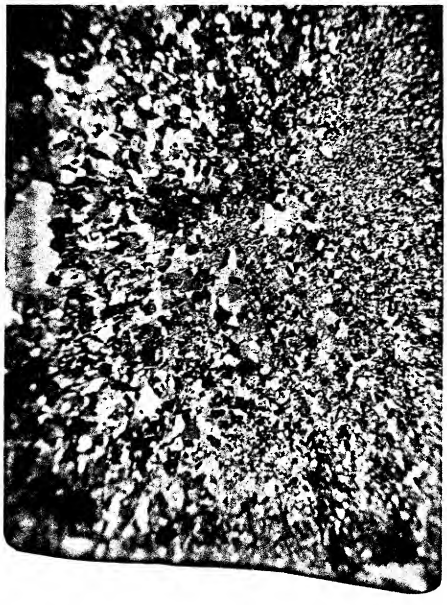

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NOTE.—The sections, 1 to 22, are all from bars which were cast, in heated moulds, and fractured by longitudir
In some cases (Nos. 7, 8, 19–22) the sections were also annealed by heating th

No. 1. Gold alloyed with 0·2 °/₀ of Zirconium. × 17 diam. Illuminated obliquely.

No. 2. Gold alloyed with 0·2 °/₀ of Lithium. × 17 diam. Illuminated obliquely.

No. 3. Gold alloyed with 0·2 °/₀ of Indium. × 17 diam. Illuminated obliquely.

No. 6. Same as No. 1, but illuminated from the opposite direction.

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No. 8. Gold alloyed with 0·2 °/₀ of Antimony. Annealed. × 17 diam. Illuminated obliquely.

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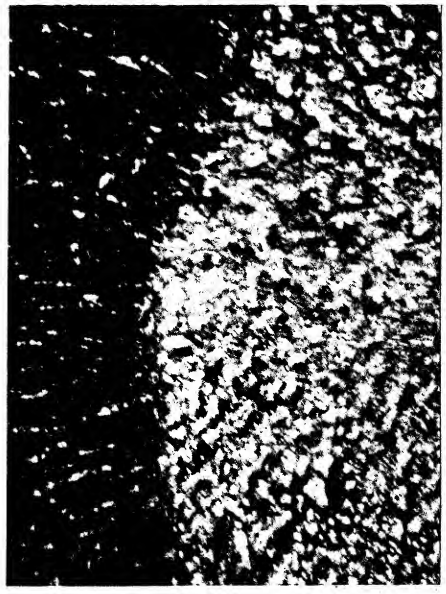

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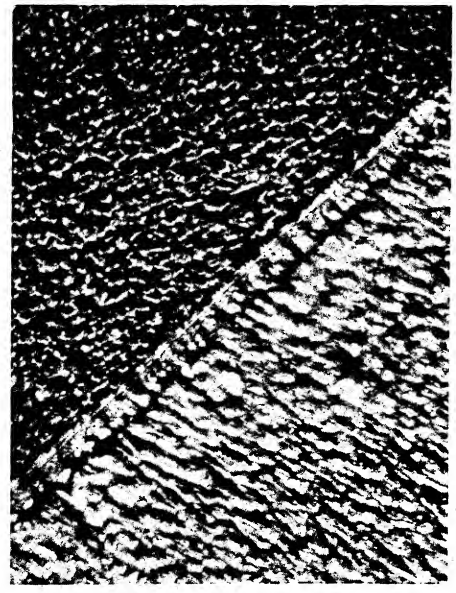

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*Phototypie Berthaud, Paris.*

ɔngitudinal stress. In all cases, except Nos. 16, 18, they were etched with *aqua regia*.
ɜating them to a temperature between 200° and 250° C.

·2 °/₀ of Illumi-

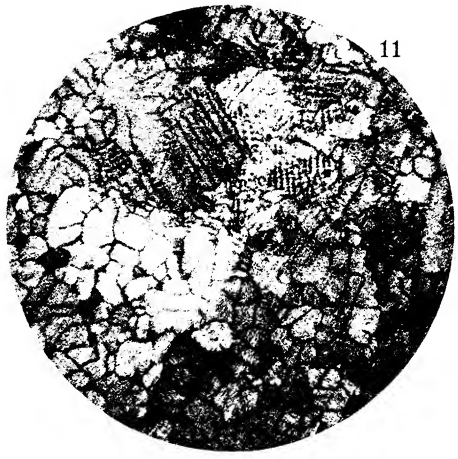
No. 4. Gold alloyed with 0·2 °/₀ of Aluminium. × 17 diam. Illuminated obliquely.

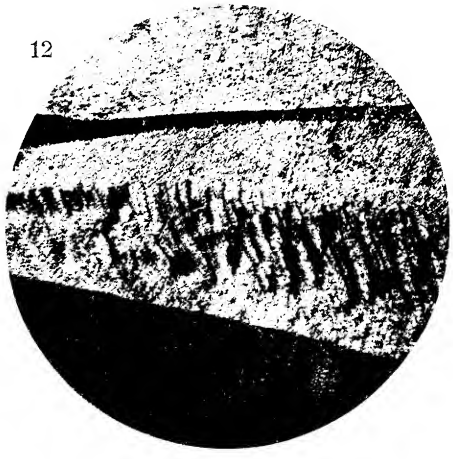
No. 5. Gold alloyed with 0·2 °/₀ of Potassium. × 17 diam. Illuminated obliquely.

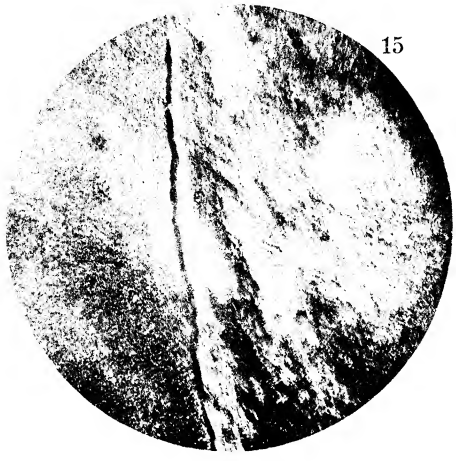
·2 °/₀ of × 17 quely.

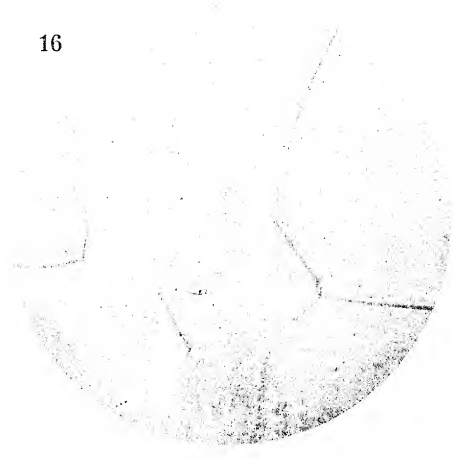
No. 9. Gold alloyed with 0·2 °/₀ of Rhodium. × 1000 diam. Illuminated perpendicularly.

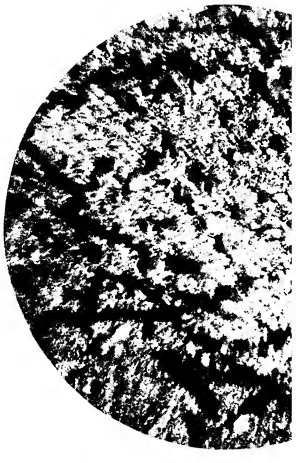
No. 10. Pure Gold. × 1000 diam. Illuminated perpendicularly.

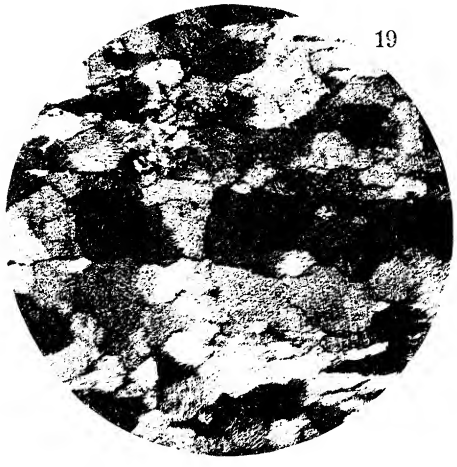


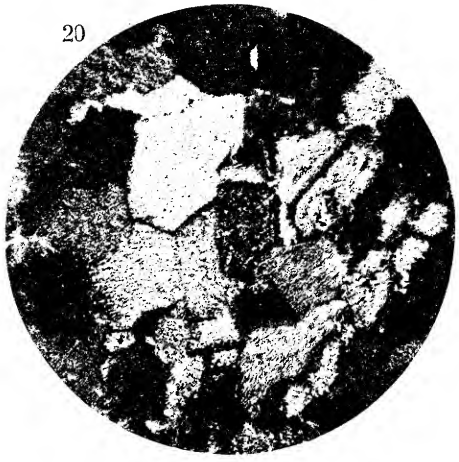







No. 11. Gold alloyed with 0·2 °/₀ of Potassium. × 150 diam. Illuminated perpendicularly.

No. 12. Gold alloyed with 0·2 °/₀ of Rhodium. × 150 diam. Illuminated perpendicularly.

No. 13. Gold alloyed wi Aluminium. × 150 d nated perpendicularly.

No. 15. Gold alloyed with 0·2 °/₀ of Thallium. × 150 diam. Illuminated perpendicularly.

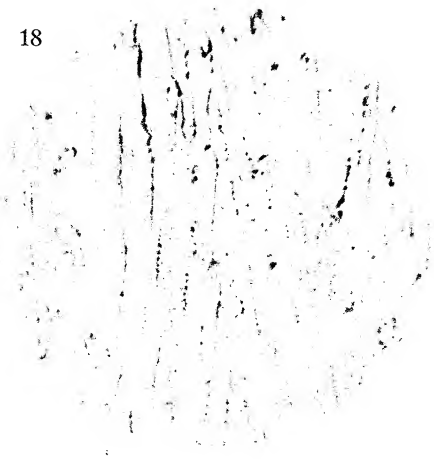
No. 16. Pure Gold. Etched with sulphuric acid. × 150 diam. Illuminated perpendicularly.

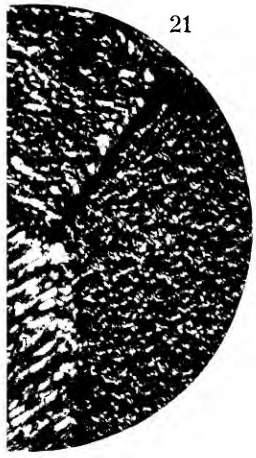
No. 17. Gold alloyed wit Indium. × 500 diam. perpendicularly.

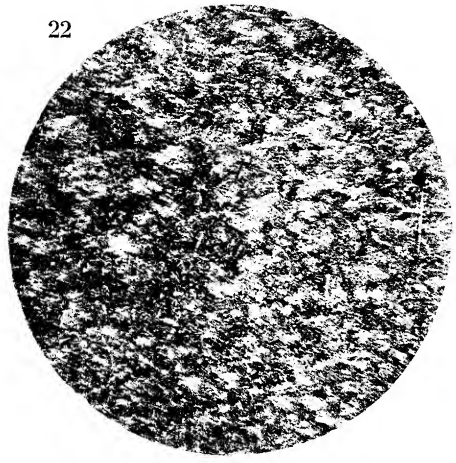
No. 19. Gold alloyed with 0·2 °/₀ of

No. 20. Gold alloyed with 0·2 °/₀ of Bis-

No. 21. Gold alloyed with




*Phototypie Berthaud, Paris.*

)yed with 0·2 °/₀ of × 150 diam. Illumi- cularly.

No. 14. Gold alloyed with 0·2 °/₀ of Indium. × 150 diam. Illuminated perpendicularly.

)yed with 0·2 °/₀ of )0 diam. Illuminated r.

No. 18. Gold alloyed with 0·2 °/₀ of Indium. Etched with nitric acid. × 150 diam. Illuminated perpendicularly.

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No. 22. Gold alloyed with 0·2 °/₀ of

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No. 19. Gold alloyed with 0·2 °/₀ of Thallium. Annealed. × 150 diam. Illuminated perpendicularly.

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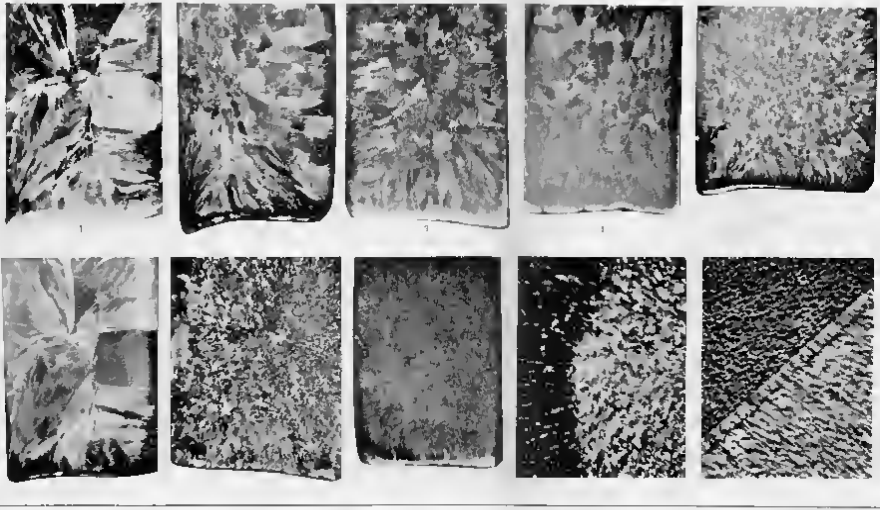
× 150 diam. Illuminated perpendicularly.

No. 22. Gold alloyed with 0·2 °/₀ of Antimony. Annealed. × 150 diam. Illuminated perpendicularly.



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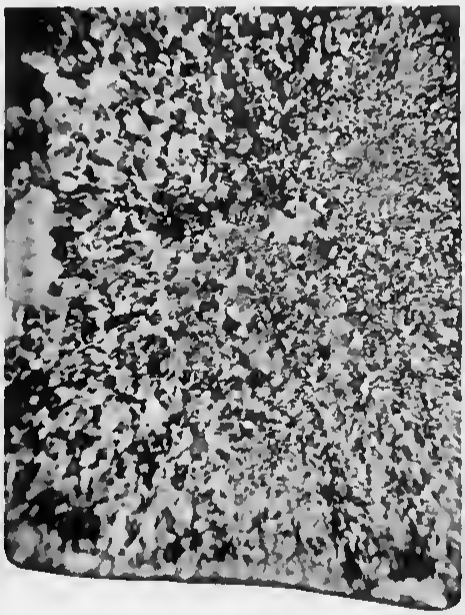

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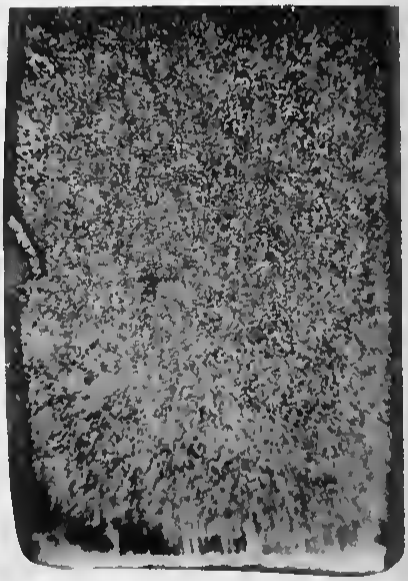

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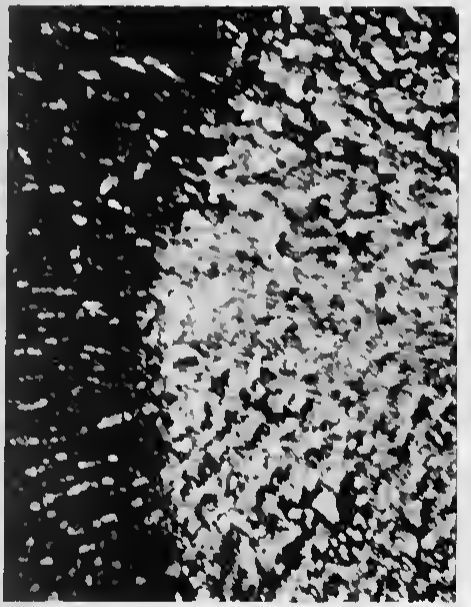

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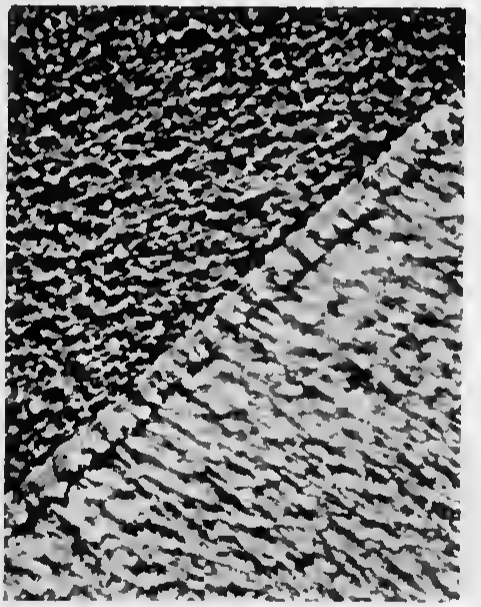

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*Phototypie Berthaud, Paris.*

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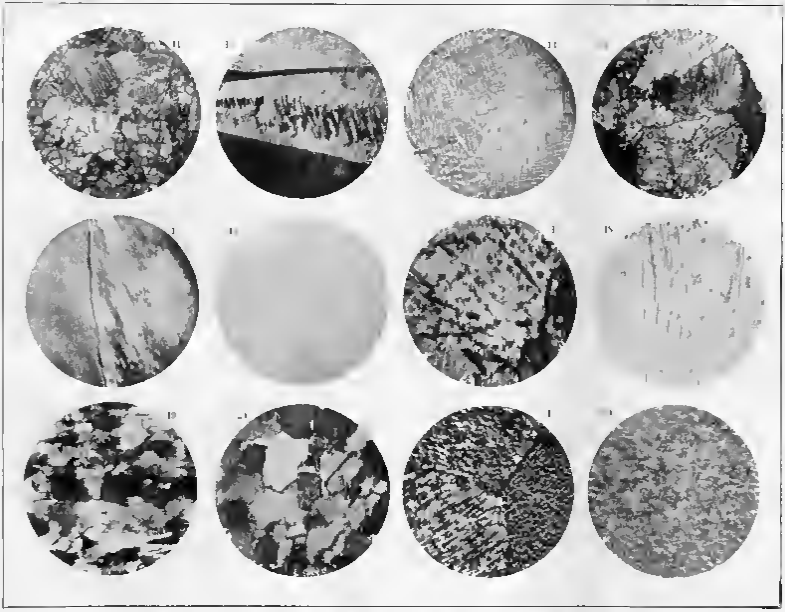


Photographs Bertram

No 11 Gold alloyed with 0 [illegible] of Potassium × 150 diam Illuminated perpendicularly

No 15 Gold alloyed with 0·2 % of Thallium × 150 diam Illuminated perpendicularly

No 19 Gold alloyed with 0·9 % of Thallium Annealed × 150 diam Illuminated perpendicularly

No 1[illegible] Gold alloyed [illegible] Rhodium × 1[illegible] [illegible] nated perpendicularly

No 19 Pure Gold [illegible] plume acid × 1[illegible] [illegible] nated perpendicularly

No 20 Gold alloyed with 0·[illegible] of Bismuth Annealed × 150 diam Illuminated perpendicularly

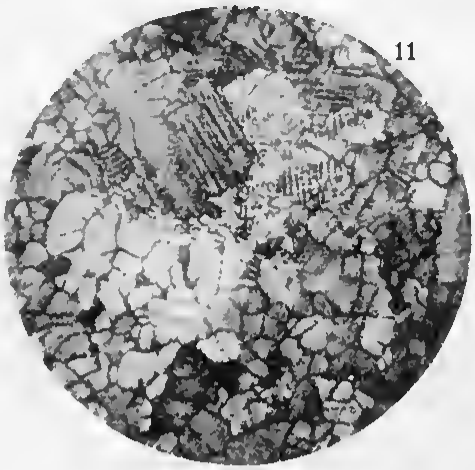
[illegible] perpendicularly

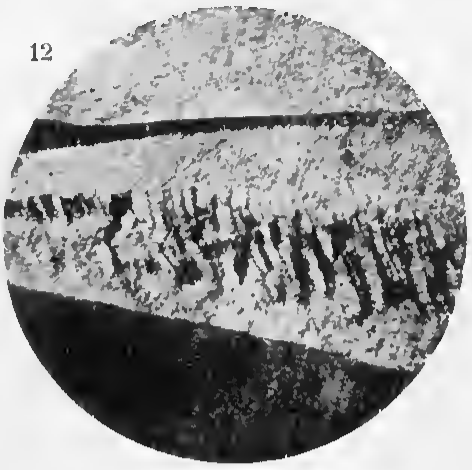
No 21 Gold alloyed [illegible] mith Annealed [illegible] Illuminated perpendicularly

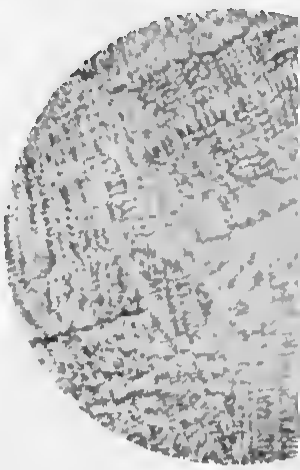
[illegible] 11 [illegible] alloyed with 0·2 % of [illegible] × 150 diam Illuminated perpendicularly

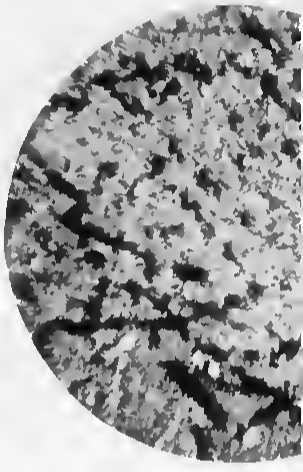
[illegible] 18 Gold alloyed with 0·2 % of [illegible] Etched with nitric acid × 1[illegible] diam Illuminated perpendicularly

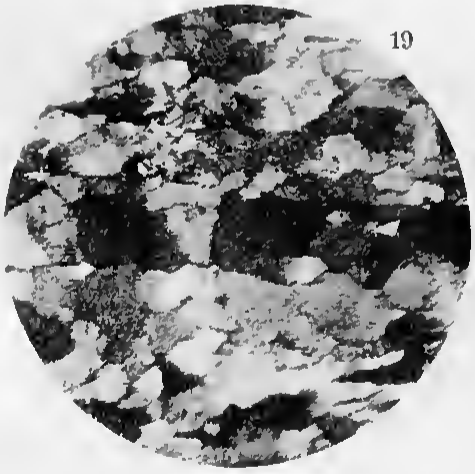
[illegible] Gold alloyed with 0·2 % of Antimony Annealed × 150 diam Illuminated perpendicularly

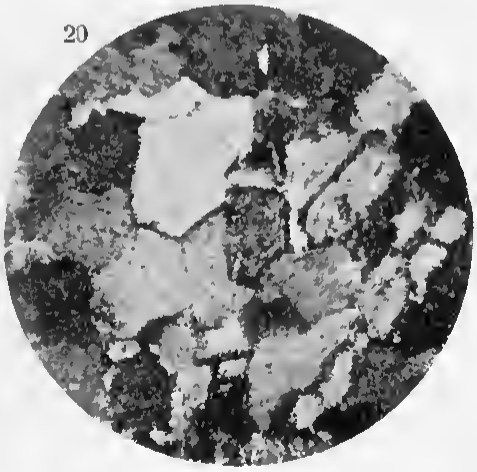


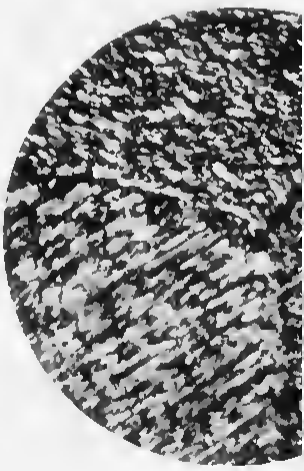







No. 11. Gold alloyed with 0·2 °/₀ of Potassium. × 150 diam. Illuminated perpendicularly.

No. 12. Gold alloyed with 0·2 °/₀ of Rhodium. × 150 diam. Illuminated perpendicularly.

No. 13. Gold alloyed wi Aluminium. × 150 d nated perpendicularly.

No. 15. Gold alloyed with 0·2 °/₀ of Thallium. × 150 diam. Illuminated perpendicularly.

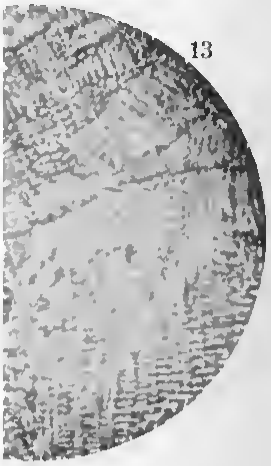
No. 16. Pure Gold. Etched with sulphuric acid. × 150 diam. Illuminated perpendicularly.

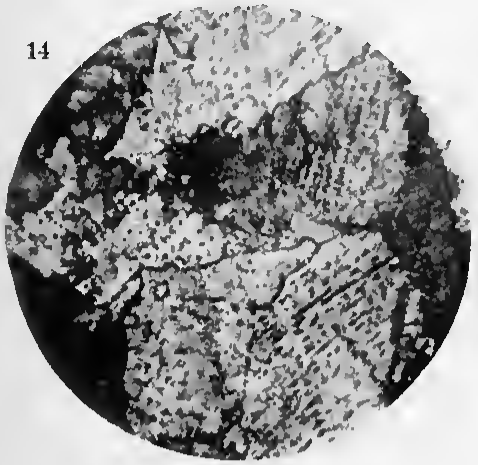
No. 17. Gold alloyed wi Indium. × 500 diam. perpendicularly.

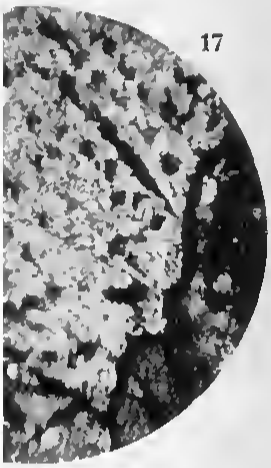
No. 19. Gold alloyed with 0·2 °/₀ of

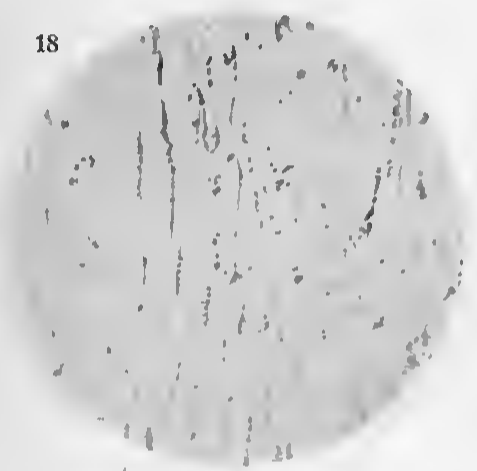
No. 20. Gold alloyed with 0·2 °/₀ of Bis-

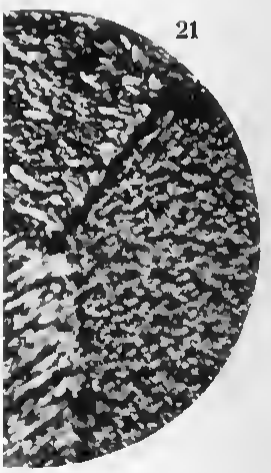
No. 21. Gold alloyed with

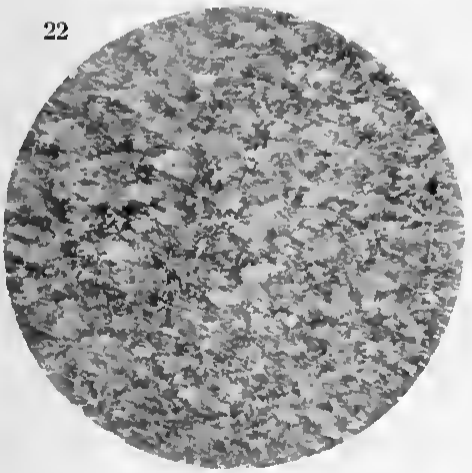



*Phototypie Berthaud, Paris.*

oyed with 0·2 °/₀ of
× 150 diam. Illumi-
ıcalarly.

No. 14. Gold alloyed with 0·2 °/₀ of Indium. × 150 diam. Illuminated perpendicularly.

oyed with 0·2 °/₀ of
)0 diam. Illuminated
y.

No. 18 Gold alloyed with 0·2 °/₀ of Indium. Etched with nitric acid. × 150 diam. Illuminated perpendicularly.

ed with 0·2 °/₀ of Bis-

No. 22. Gold alloyed with 0·2 °/₀ of

nated perpendicularly.

nated perpendicularly.

perpendicularly.

No. 19. Gold alloyed with 0·2 °/₀ of Thallium. Annealed. × 150 diam. Illuminated perpendicularly.

No. 20. Gold alloyed with 0·2 °/₀ of Bismuth. Annealed. × 150 diam. Illuminated perpendicularly.

No. 21. Gold alloyed with muth. Annealed. × Illuminated perpendicu

50 diam. Illuminated
y.

ed with 0·2 °/₀ of Bis-
aled. × 1000 diam.
rpendicularly.

Iridium. Etched with nitric acid.
× 150 diam. Illuminated perpendicularly.

No. 22. Gold alloyed with 0·2 °/₀ of Antimony. Annealed. × 150 diam. Illuminated perpendicularly.